

Heat Capacity; Heats of Fusion, Vaporization, and Transition; and Vapor Pressure of *N*-Dimethylaminodiborane, $(\text{CH}_3)_2\text{NB}_2\text{H}_5$

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The heat capacity of *N*-dimethylaminodiborane was determined in the temperature range from 17° to 285°K by means of an adiabatic calorimeter. A first-order solid-solid transition was found at $199.9 \pm 0.1^\circ\text{K}$, with a latent heat of $7794 \text{ abs j mole}^{-1}$. The triple-point temperature was found to be $218.4 \pm 0.2^\circ\text{K}$, and the heat of fusion to be $1,408 \pm 30 \text{ abs j mole}^{-1}$. The measurements of the heat of vaporization at 271.60°K (94.3 mm Hg) yielded $30,119 \pm 30 \text{ abs j mole}^{-1}$. The results of the vapor-pressure measurements from 220° to 290°K can be represented by the equation

$$\log_{10} p_{\text{mmHg}} = 406.5734/T + 5.2095614 \times 10^{-2} T + 1.01048 \times 10^{-5} T^2 - 1.390588 \times 10^{-7} T^3 - 11.63086.$$

The data were used to construct a table of smoothed values of heat capacity, enthalpy, entropy, and Gibbs free energy from 0° to 285°K. The entropy of *N*-dimethylaminodiborane in the ideal gas state at 1 atm and 271.60°K was computed from the data to be $302.3 \pm 0.6 \text{ abs j deg}^{-1} \text{ mole}^{-1}$ ($72.25 \pm 0.14 \text{ cal deg}^{-1} \text{ mole}^{-1}$).

1. Introduction

Many boron hydrides and other boron-containing compounds are relatively unstable and undergo various disproportionation reactions. These equilibria are complicated in many cases by the large number of different compounds produced in the reaction. The dearth of thermodynamic information regarding these substances prevents computation of the degree of thermal and chemical stability. Also, there is considerable interest in these materials from the standpoints of their structure and of practical applications. In view of these considerations, a program of thermodynamic study was initiated to aid in the better understanding of boron-containing compounds. This paper deals with the determination of heat capacity, heats of fusion, vaporization, and transition, and vapor pressure, and with the computation of the thermal properties of *N*-dimethylaminodiborane, $(\text{CH}_3)_2\text{NB}_2\text{H}_5$.

2. Apparatus and Method

Measurements of the heat capacity and the heats of fusion and transition were carried out in an adiabatic calorimeter similar in design to that described by Southard and Brickwedde [1]¹. The details of the design and operation of the calorimeter have been previously given by Scott et al. [2].

In the measurements of the gross (sample plus container) heat capacities at the lower temperatures, where the heat-capacity curve has a large curvature, the temperature interval of heating, ΔT , was made small in order to minimize the curvature correction; from 17° to 30°K ΔT was 1 to 3 deg, from 30° to 60°K it was increased from 3 to 5 deg, and above

60°K it was as much as 8 deg. Also, in the transition range (discussed in section 4 of this paper) ΔT was made small to obtain as closely as possible the shape of the heat-capacity curve, as well as to minimize the curvature correction. The curvature corrections [2] were made whenever significant using the relation

$$Z_{T_m} = \frac{Q}{\Delta T} - \left(\frac{\partial^2 Z}{\partial T^2} \right)_{T_m} \frac{(\Delta T)^2}{24} \dots, \quad (1)$$

where Z is the heat capacity, T_m the mean temperature of the temperature interval ΔT , and Q the energy input. The net heat capacities were obtained by subtracting the tare (empty container) heat capacities from the gross heat capacities after the necessary curvature corrections have been made. The tare heat capacities at the temperatures of the observed gross heat capacities were obtained by four-point Lagrangian interpolation [3] in a table of smoothed tare heat capacities given at 1-deg intervals.

At the higher temperatures, where the vapor pressure became significant, corrections were applied to the net heat capacities for the heat of vaporization and for the mass of vapor in the filling tube. The corrections were determined by using the following relation [4]

$$C_{\text{satd}} = M \frac{C_{\text{net}} - T_m \frac{d}{dT} \left\{ \frac{dp}{dT} [V - (m - m_t) v_c] \right\} - l \frac{dm_t}{dT}}{m - m_t}, \quad (2)$$

where C_{satd} is the molal heat capacity of the condensed phase at saturation pressure, M the molecular weight of the material, C_{net} the net heat capacity, p the vapor pressure at T_m , V the volume of the calo-

¹ Figures in brackets indicate the literature references at the end of this paper.

rimeter, m the total mass of sample, m_i the mass of vapor in the filling tube, v_c the specific volume of the condensed phase, and l the heat of vaporization of unit mass of sample at T_m . This correction at the highest temperature (285°K) of the measurements amounted to 0.15 percent.

The heat-of-vaporization experiments were made in another adiabatic calorimeter similar in design to those described by Osborne and Ginnings [5] and by Aston et al. [6]. The details of the design and operation can be found in these references.

For the vapor-pressure measurements, the calorimeter used in the heat-capacity experiments was connected to a mercury manometer, which was read by means of a mirror-backed calibrated glass scale. The calorimeter served as a thermostated container, and the vapor-pressure measurements were generally made at successively higher temperatures. As no provision was made to stir the sample, several measurements were made at successively lower temperatures as a check on the equilibrium of the sample. These two series of results, one obtained going up and the other going down the temperature scale, did not differ significantly. The pressure readings were converted to standard mm Hg ($g = 980.665 \text{ cm sec}^{-2}$, temperature = 0°C) on the basis that the local gravity is $980.076 \text{ cm sec}^{-2}$.

Temperatures above 90°K were determined in accordance with the International Temperature Scale [7]. Below 90°K, a provisional scale was used, which is based on a set of platinum resistance thermometers calibrated against a helium-gas thermometer [8]. All electrical instruments and accessory equipment were calibrated at the Bureau. The atomic weights used were based on the values given in the 1952 Report of the Committee on Atomic Weights of the American Chemical Society [9].

3. Sample and Its Purity and Heat of Fusion

About 200 ml of the material was originally received in a break-seal ampoule; after degassing, by repeated freezing, pumping, and melting, approximately one-half of this material was transferred by vacuum distillation into a weighing flask for calorimetric studies. The sample in the weighing flask was degassed further, first by pumping at about -70°C and later by freezing, pumping, and melting three times. Following this treatment the sample (59.0725 g) was transferred immediately into the calorimeter.

The purity of the sample was determined prior to the heat-capacity measurements from its equilibrium melting temperatures. In this method all the impurity is assumed to remain in the liquid phase and not to form a solid solution with *N*-dimethylaminodiborane, and Raoult's law of solution is assumed to be applicable throughout the whole range of impurity concentration. The observed equilibrium melting temperatures are plotted versus the reciprocal of the corresponding fractions of the material melted, $1/F$. The fraction melted is obtained from the energy input, heat capacity, and heat of fusion. The product

of the cryoscopic constant, $\Delta H_f/RT_p^2$, and the slope of the temperature versus $1/F$ curve is the mole fraction impurity. In the cryoscopic constant, ΔH_f is the heat of fusion, R the gas constant, and T_p the triple-point temperature. The extrapolated temperature intercept (at $1/F=0$) of the temperature versus $1/F$ plot is taken as the triple-point temperature of the pure material. The results of the measurements and subsequent computation are summarized in table 1. The cryoscopic constant used was 0.0036 deg^{-1} .

TABLE 1. *Equilibrium melting temperatures of N-dimethylaminodiborane*

Mole fraction impurity = $0.0036 \Delta T$,
°K = °C + 273.16°

Reciprocal of fraction melted, $1/F$	T
7.50	°K
4.89	^a 217.2538
3.39	217.5751
2.51	217.7886
1.42	217.9303
0.00	218.1683
	^b 218.4
Triple-point temperature, $218.4 \pm 0.2^\circ \text{K}$. Purity, 99.94 mole percent.	

^aThe temperatures given are accurate to 0.01°K. Whenever temperatures are expressed to the fourth decimal, the last two figures are significant only in the measurement of small temperature differences.

^bExtrapolated.

The heat of fusion was determined in the usual manner by heating continuously from a temperature a few degrees below the triple-point temperature to just above it and by correcting for heat capacity and for premelting caused by the presence of impurity. (Certain amounts of material are already melted at temperatures just below the triple-point temperature. The amount melted is dependent upon the impurity content, the cryoscopic constant, and the closeness of the temperature to the triple-point temperature.) The experimental heat capacities in the region just below the triple-point temperature were found to have apparently high values caused by the premelting of the sample. The premelting corrections calculated from the impurity content did not seem to correct the observed heat capacities satisfactorily. The final values of heat capacity in this region (see table 6) were obtained after revising the observed values by a combination of premelting correction and extrapolation. These corrections were not particularly accurate, consequently the heat capacities are believed to have large errors, probably as much as several percent. The calculated value of the heat of fusion, which is relatively small, has a large percentage uncertainty resulting from the inaccuracies in the heat capacity and premelting corrections.

The results of the heat-of-fusion measurements and computations are summarized in table 2. Considering the various known sources of uncertainties, such as premelting and heat capacity corrections mentioned in the previous paragraph, energy measurements, heat leaks, and mass of sample, the heat of fusion is probably accurate to $\pm 30 \text{ abs j mole}^{-1}$.

TABLE 2. Molal heat of fusion of *N*-dimethylaminodiboraneMolecular weight = 70.756, triple-point temperature = 218.4°K
°K = °C + 273.16°

Temperature interval	Heat input	Corrections ^a		ΔH_f
		Heat capacity	Premelting	
K°	<i>abs j mole⁻¹</i>	<i>abs j mole⁻¹</i>	<i>abs j mole⁻¹</i>	<i>abs j mole⁻¹</i>
214.2928 to 221.3568 ^a	2298.1	-953.3	61.0	1405.8
215.1552 to 220.2458	2008.0	-685.4	77.2	1399.8
214.8542 to 221.2065	2210.0	-859.6	70.6	1421.0
213.7353 to 221.5915	2408.3	-1058.4	53.7	1403.6
Mean				1407.6
Standard deviation of the mean				± 4.7 ^b
Estimated uncertainty				± 30

^a The temperatures given are accurate to $\pm 0.01^\circ\text{K}$. Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

^b Standard deviation of the mean as used here and in table 4 is defined as $[\sum d^2/n(n-1)]^{1/2}$, where d is the difference between a single observation and the mean, and n is the number of observations.

4. Heat Capacity and Heat of Transition

Measurements of the heat capacity were made from about 17° to 285° K; corrections for curvature (see eq 1) and vaporization (see eq 2) were applied to the observed values wherever significant. The equation for the liquid density reported by Burg and Randolph [10], based on their experimental measurements, was used in making the vaporization corrections. The density equation was extended below its experimental temperature range whenever required. As the corrections become smaller at lower temperatures (at the highest temperature of the measurements, 285° K, the vaporization correction was 0.15 percent of the net heat capacity), the error in the extrapolation is considered to have negligible effect on the final observed heat-capacity values given in table 3 and figure 1.

The values given in table 3, although corrected for vaporization and curvature wherever significant, have not been corrected for premelting in the region just below the triple-point temperature. As mentioned in section 3, considerable premelting effects were observed in the apparently high values of heat capacity. In calculating the final smoothed values of heat capacities given in table 6 of section 7, the observed values were first revised by a combination of premelting correction and extrapolation. The revisions made are believed to be highly inaccurate, consequently the uncertainty in the heat capacity of this region may be as high as several percent. At other regions of temperature, except below about 60° K, the heat capacity is probably accurate to ± 0.2 percent. Below 60° K the probable error in the values is believed to increase to about 1 percent largely due the smaller temperature interval of heating, smaller energy input, and decreased sensitivity of the thermometer.

Because of the relatively low heat of fusion and the large premelting effect observed, the solid-solid transition occurring between 195° and 205° K was originally thought to arise from the melting of a eutectic mixture. A close examination of the heat capacity between 200° K and the triple-point tem-

TABLE 3. Observed heat capacity of *N*-dimethylaminodiborane

Molecular weight = 70.756, °K = °C + 273.16°

T_m^a	ΔT	C_{std}
RUN 1		
$^\circ K$	$^\circ K$	<i>abs j deg⁻¹ mole⁻¹</i>
207.7381 ^b	1.6866	125.62
209.4220	1.6811	126.16
211.2787	2.0324	127.52
213.2921	2.0014	129.45
215.2246	1.8635	146.63
216.7813	1.2500	271.62 ^c
217.8016	0.7906	1090.6 ^c
219.7768	3.1599	260.51 ^c
222.8033	2.8930	142.60
225.6900	2.8803	143.31
RUN 2		
213.7044	2.9016	133.85
215.9800	1.6496	175.53
217.0293	0.4490	283.33 ^c
217.4144	.3213	435.26 ^c
217.6818	.2135	710.27 ^c
217.8594	.1417	1125.4 ^c
218.0493	.2380	1868.1 ^c
219.2070	2.0775	334.84 ^c
221.0258	1.5599	142.39
RUN 3		
221.4889	1.1212	142.48
222.6082	1.1173	142.79
225.4610	4.5204	143.45
230.2422	5.0420	144.64
235.2658	5.0053	145.84
240.2574	4.9779	147.10
245.2123	4.9318	148.45
250.1228	4.8891	149.76
254.9938	4.8530	151.13
RUN 4		
90.0286	2.1671	59.266
93.6566	5.0887	61.123
98.6392	4.8765	63.660
104.0464	4.5293	66.449
108.8120	5.0019	68.925
115.3404	8.0549	72.254
123.2074	7.6791	76.304
130.7321	7.3702	80.148
137.9640	7.0936	83.826
144.9421	6.8626	87.357
151.7720	6.7973	90.867
158.4743	6.6072	94.374
RUN 5		
160.7098	6.5065	95.657
167.1356	6.3451	99.198
173.3990	6.1939	102.63
179.5152	6.0384	106.54
185.4870	5.4870	110.43
191.3747	5.8702	115.28
196.9508	5.2820	138.82
199.7366	0.2896	4359.1 ^c
RUN 6		
189.8876	2.9971	113.53
194.2642	5.7560	118.91
198.4696	2.6549	379.67 ^c
199.8516	0.1089	11730 ^c
199.9228	.0337	38081 ^c
199.9497	.0200	96316 ^c
201.2234	2.5273	1155.1 ^c
203.3206	1.6672	124.69
RUN 7		
202.3303	1.6582	124.25
204.8100	3.3011	124.70
210.6664	8.3755	126.85
218.0304	6.3523	347.90 ^c
222.4840	2.5551	142.70

TABLE 3. Observed heat capacity of *N*-dimethylaminodiborane—Continued

Molecular weight = 70.756, °K = °C + 273.16°

T_m^a	ΔT	C_{satd}
RUN 8		
°K	°K	abs j deg ⁻¹ mole ⁻¹
190.2736	4.1895	113.94
194.4084	4.0799	119.06
199.1227	5.3488	1573.3 °
203.0568	2.5193	124.82
205.5710	2.5092	125.47
210.2804	6.9097	127.06
217.6634	7.8562	306.55°
RUN 9		
17.5414	1.6646	7.864
19.0626	1.3777	9.434
20.3464	1.1901	10.821
21.7180	1.5530	12.282
23.1742	1.3594	13.830
24.4628	1.2179	15.299
26.4766	2.8095	17.414
29.3340	2.9055	20.328
32.3968	3.2200	23.325
35.7151	3.4166	26.400
39.4570	4.0671	29.444
44.5193	6.0576	33.154
50.1185	5.1408	36.970
55.5076	5.6373	40.288
61.3216	5.9909	43.719
67.0340	5.4338	47.017
73.2088	6.9159	50.598
79.8362	6.3387	53.844
86.2264	6.4418	57.397
93.0664	7.7382	60.922
RUN 10		
247.2118	6.1379	149.19
252.7154	4.8691	150.72
257.5652	4.8305	152.10
263.5702	7.1796	153.73
270.7090	7.0979	155.98
277.8226	7.1295	158.20
284.9132	7.0515	160.74

^a T_m is the mean temperature of the heating interval.

^b The temperatures given are accurate to $\pm 0.01^\circ$ K. Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

^c These are apparently high values obtained in the temperature region of the solid-solid transition and the triple point.

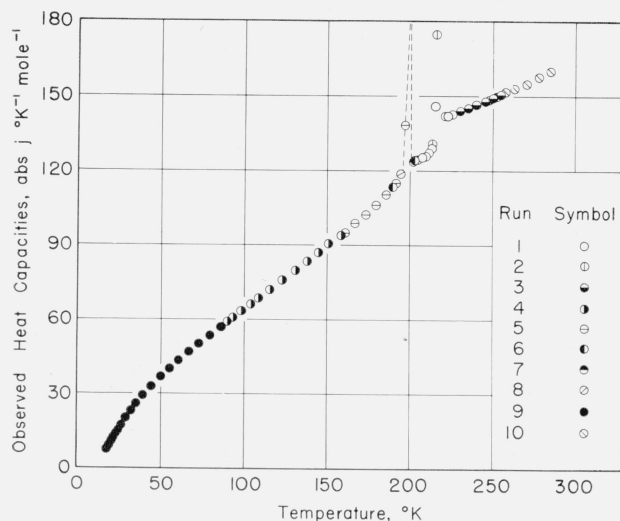


FIGURE 1. Observed heat capacity of *N*-dimethylaminodiborane.

perature suggested, however, that the discontinuity in the heat capacity is probably from a solid-solid transition. The transition was found to involve a large latent heat. The enthalpy change from 190° to 205° K was determined, in which two measurements from runs 6 and 8 (see tables 3 and 7) gave 9570.4 and 9573.8 abs j mole⁻¹, respectively. These values were obtained by summing the various input energies in this temperature range and by correcting to the even temperature interval. The results of the heat-capacity measurements (see table 3, runs 6 and 8) suggest that the peak or the transition temperature is $199.9 \pm 0.1^\circ$ K. The latent heat associated with the transition was estimated from the enthalpy change from 190° to 205° K and the extrapolated heat capacity in this region to be 7794 abs j mole⁻¹.

5. Heat of Vaporization

The heat-of-vaporization experiments were made at 271.60° K (94.3 mm Hg). The experimentally determined quantity γ , the energy input per mole of sample collected [11], is related to the molal heat of vaporization ΔH_v , by the expression

$$\Delta H_v = \gamma - T\mathcal{U} \frac{dp}{dT} \quad (3)$$

where \mathcal{U} is the molal volume of the liquid, T the absolute temperature of vaporization, and p the vapor pressure. The molal volume of the liquid was obtained by extrapolating, a few degrees, the density equation (0° to 25° C) given by Burg and Randolph [10]. The temperature derivative of the vapor pressure, dp/dT , was obtained by differentiating with respect to temperature the vapor-pressure equation (eq 4). The results of the heat-of-vaporization measurements and computations are summarized in table 4. Considering various known sources of error and the precision of the measurements, a probable error of ± 30 abs j mole⁻¹ is assigned to the heat of vaporization.

TABLE 4. Heat of vaporization of *N*-dimethylaminodiborane at 271.60° K

Molecular weight = 70.756, pressure = 94.3 mm Hg
°K = °C + 273.16°

γ	$T\mathcal{U}(dp/dT)$	ΔH_v
abs j mole ⁻¹	abs j mole ⁻¹	abs j mole ⁻¹
30,144	18	30,126
30,127	18	30,109
30,141	18	30,123
Mean.....		30,119
Standard deviation of the mean.....		$\pm 5^a$
Estimated uncertainty.....		± 30

^a See footnote b, table 2.

The heat of vaporization computed in accordance with the Clapeyron equation gave 29,900 abs j mole⁻¹, which is in fair agreement with the experimental value obtained. In the computation the vapor was assumed to follow the Berthelot equation of state, the constants ($T_c = 485^\circ$ K and $p_c = 36$ atm) of which

were estimated according to $T_b=2/3T_c$ and the method described by Walden [12], respectively. The sources of the dp/dT and the molal volume of the liquid phase were those mentioned in the previous paragraph.

6. Vapor Pressure

The results of the vapor-pressure measurements, made from about 220° to 290°K, can be represented by the equation

$$\log_{10} p_{\text{mm Hg}} = 406.5734/T + 5.2095614 \times 10^{-2}T + 1.01048 \times 10^{-5}T^2 - 1.390588 \times 10^{-7}T^3 - 11.63086. \quad (4)$$

The constants were determined by the method of least squares. In column 4 of table 5 are given the deviations of the observed values from the calculated values based on this equation. There are also given in this table the vapor-pressure results obtainable from the equation

$$\log_{10} p_{\text{mm Hg}} = -1727.64/T + 1.75 \log_{10} T - 0.004661T + 5.3370, \quad (5)$$

reported by Burg and Randolph [10] based on their experimental results from about -36° to 50° C.

Attempts were made to carry out vapor-pressure measurements at higher temperatures in an isoteniscope. However, it was found that even at 300°K the vapor pressure increased, presumably due to decomposition, over an extended time in the isoteni-

TABLE 5. Vapor pressure of *N*-dimethylaminodiborane

°K=°C+273.16°

<i>T</i>	<i>p</i> , obs	<i>p</i> , calc ^a	Δ <i>p</i> , obs-calc	<i>p</i> , [10]
SERIES I				
°K	mm Hg	mm Hg	mm Hg	mm Hg
234.71-----	12.1	12.2	-0.1	10.7
237.51-----	14.8	14.5	+3	13.0
242.75-----	19.8	19.8	0	18.3
245.57-----	23.8	23.3	+5	21.9
249.29-----	29.0	28.9	+1	27.5
256.48-----	43.2	43.1	+1	41.8
261.95-----	57.7	57.8	-1	56.6
264.86-----	67.3	67.2	+1	66.1
268.89-----	82.4	82.5	-1	81.4
271.33-----	92.8	93.1	-3	92.0
273.50-----	103.5	103.5	0	102.4
283.22-----	162.5	162.4	+1	161.5
287.18-----	193.3	193.0	+3	192.4
SERIES II				
219.79-----	4.8	4.8	0	3.6
227.78-----	7.8	8.0	-2	6.6
236.55-----	13.5	13.7	-2	12.2
248.82-----	28.4	28.1	+3	26.7
255.98-----	41.6	41.8	-3	40.7
258.91-----	49.0	49.1	-1	47.8
260.53-----	53.8	53.6	+2	52.4
266.54-----	73.0	73.2	-2	72.1
SERIES III				
218.28-----	4.4	4.4	0	3.2
226.05-----	7.3	7.2	+1	5.8
245.19-----	22.5	22.8	-3	21.4
260.15-----	52.3	52.5	-2	51.3

^a Equation (4).

scope. The average increase over several days was about 0.01 mm Hg per hour at this temperature. Consequently, the results with the isoteniscope have not been considered in this paper.

7. Derived Thermal Properties

Empirical equations were fitted to the observed heat capacities and the deviations from the equa-

TABLE 6. Heat capacity, enthalpy, entropy, and Gibbs free energy of *N*-dimethylaminodiborane

Molecular weight=70.756, °K=°C+273.16°

<i>T</i>	<i>C</i> _{satd}	(<i>H</i> _{<i>T</i>} - <i>H</i> _{0°K}) _{satd}	(<i>S</i> _{<i>T</i>} - <i>S</i> _{0°K}) _{satd}	-(<i>F</i> _{<i>T</i>} - <i>H</i> _{0°K}) _{satd}
°K	abs <i>J deg</i> ⁻¹ mole ⁻¹	abs <i>J mole</i> ⁻¹	abs <i>J deg</i> ⁻¹ mole ⁻¹	abs <i>J mole</i> ⁻¹
0	0	0	0	0
5	0.213	0.2671	0.0712	0.0890
10	1.701	4268	5692	1.424
15	5.332	20.96	1.874	7.145
20	10.43	60.00	4.081	21.63
25	15.86	125.7	6.990	49.02
30	20.99	218.0	10.34	92.24
35	25.77	335.1	13.94	152.9
40	29.86	474.4	17.66	231.9
45	33.50	632.9	21.39	329.5
50	36.90	809.0	25.09	445.7
55	40.08	1002	28.76	580.4
60	42.94	1209	32.37	733.3
65	45.84	1431	35.93	904.0
70	48.77	1668	39.43	1092
75	51.54	1919	42.89	1298
80	53.93	2182	46.29	1521
85	56.68	2459	49.64	1761
90	59.34	2749	52.96	2018
95	61.84	3052	56.24	2291
100	64.37	3367	59.47	2580
105	66.94	3696	62.67	2885
110	69.51	4037	65.85	3207
115	72.09	4391	68.99	3544
120	74.66	4758	72.12	3897
125	77.22	5137	75.22	4265
130	79.78	5530	78.30	4649
135	82.32	5935	81.35	5048
140	84.85	6353	84.39	5462
145	87.39	6784	87.42	5892
150	89.95	7227	90.42	6336
155	92.56	7683	93.41	6796
160	95.24	8153	96.39	7270
165	98.00	8636	99.37	7760
170	100.7	9132	102.33	8264
175	103.6	9643	105.29	8783
180	106.8	10169	108.26	9317
185	110.2	10711	111.23	9866
190	113.7	11272	114.21	10428
195	-----	-----	-----	-----
200	-----	-----	-----	-----
205	124.8	20842	162.14	12396
210	126.6	21477	165.20	13214
215	129.1	-----	-----	-----
218.4 ^a	131.2	-----	-----	-----
Liquid				
218.4 ^a	141.9	-----	-----	-----
220	142.1	24133	177.46	14908
225	143.3	24847	180.67	15803
230	144.6	25566	183.83	16715
235	145.8	26292	186.95	17642
240	147.1	27025	190.04	18584
245	148.5	27764	193.08	19542
250	149.9	28510	196.10	20515
255	151.3	29263	199.08	21503
260	152.7	30023	202.03	22505
265	154.1	30790	204.95	23522
270	155.7	31565	207.85	24554
275	157.3	32347	210.72	25600
280	159.0	33138	213.57	26661
285	160.8	33938	216.40	27735

^a Extrapolated.

tions were plotted on a large scale. The heat capacities given in table 6 at equally spaced integral temperatures were obtained by the combination of the approximate empirical equations and the large scale deviation curves. The heat-capacity values of table 6 below 17° K were obtained by extrapolation using a Debye function fitted to experimental values between 17° and 30° K.

The enthalpy, entropy, and Gibbs free energy values were obtained by evaluating, respectively, the thermodynamic relations

$$(H_T - H_{0^\circ\text{K}})_{\text{satd}} =$$

$$\int_0^T C_{\text{satd}} dT + \Delta H_{\text{tr}} + \Delta H_{\text{f}} + \int_0^T \mathcal{V}(dp/dT)_{\text{satd}} dT, \quad (6)$$

$$(S_T - S_{0^\circ\text{K}})_{\text{satd}} = \int_0^T C_{\text{satd}} dT/T + \Delta H_{\text{tr}}/T_{\text{tr}} + \Delta H_{\text{f}}/T_{\text{tp}}, \quad (7)$$

and

$$(F_T - H_{0^\circ\text{K}})_{\text{satd}} = - \int_0^T (S_T - S_{0^\circ\text{K}})_{\text{satd}} dT + \int_0^T \mathcal{V}(dp/dT)_{\text{satd}} dT. \quad (8)$$

In these expressions ΔH_{tr} is the heat of transition, T_{tr} the temperature of transition, and \mathcal{V} the molal volume of the condensed phase. Other symbols have the usual or previously defined significance. The equations were evaluated, except between 190° and 220° K, by numerical integration using four-point Lagrangian integration coefficients [3]. Between 190° and 220° K, the enthalpy change was obtained by summing the experimental input energies in runs that were made continuously through either or both of the two first-order transitions. This procedure was particularly necessary for evaluating the enthalpy change in the temperature region that included the triple-point temperature. As mentioned in section 3, the premelting corrections were highly uncertain and, although the measurements of the total energy involved were precise, the energy distribution between melting and heat capacity may be inaccurate. In the interval from 190° to 205° K, as given in table 7, the enthalpy changes for runs 6 and 8 were 9570.4 and 9573.8 abs j mole⁻¹, respectively. From 210° to 220° K, which includes the triple-point temperature, runs 1, 7, and 8 gave 2656.1, 2657.7, and 2660.3 abs j mole⁻¹, respectively, for the enthalpy change. In run 8, the heat-capacity experiments were made continuously from 188.1789° to 221.5915° K, which gave 12861.9 abs j mole⁻¹ for the enthalpy change in the interval 190° to 220° K. Upon taking 9570.4 and 2656.1 abs j mole⁻¹, which have been obtained under optimum

experimental conditions, for the enthalpy changes for the intervals 190° to 205° K and 210° to 220° K, respectively, the enthalpy change for the interval 205° to 210° K becomes 635.4 abs j mole⁻¹.

TABLE 7. Molal enthalpy and entropy change of *N*-dimethylaminodiborane over various temperature intervals

Molecular weight = 70.756, °K = °C + 273.16°

Run	Temperature interval	ΔH	ΔS
	°K	abs j mole ⁻¹	abs j deg ⁻¹ mole ⁻¹
6-----	190 to 205	9570.4	47.923
8-----	190 to 205	9573.8	48.154
1-----	210 to 220	2656.1	12.263
7-----	210 to 220	2657.7	12.274
8-----	210 to 220	2660.3	12.297
8-----	190 to 220	12861.9	-----
8-----	205 to 210	635.4	3.062

The entropy changes for the corresponding temperature intervals (see table 7) were obtained by summing the various $\Delta H/T_m$'s, where T_m is the mean temperature of the heating interval. In the interval 190° to 205° K, runs 6 and 8 gave 47.923 and 48.154 abs j deg⁻¹ mole⁻¹, respectively. As ΔH and correspondingly the ΔT were smaller in run 6, the entropy change of this run was used in constructing table 6. For the interval 205° to 210° K, the entropy change was obtained by merely dividing the enthalpy change (635.4 abs j mole⁻¹) by the mean temperature (207.5°K). For the interval 210° to 220°K, runs 1, 7, and 8 gave 12.263, 12.274, and 12.297 abs j deg⁻¹ mole⁻¹, respectively. The value 12.263 abs j deg⁻¹ mole⁻¹ of run 1 was selected for constructing the table.

The entropy of *N*-dimethylaminodiborane in the ideal gas state at 1 atm and 271.60°K was evaluated from the data, and the computations are summarized in table 8. To make the gas-imperfection correction, the *N*-dimethylaminodiborane vapor was assumed to follow the Berthelot equation of state. The uncertainty of ± 0.6 abs j deg⁻¹ mole⁻¹ given for the entropy in the ideal-gas state was obtained by statistically combining the estimated uncertainties in the entropy of liquid *N*-dimethylaminodiborane at 271.60°K and in the entropy of vaporization. The uncertainty in the gas-imperfection correction was assumed negligible.

TABLE 8. Summary of the experimental molal entropy calculated for *N*-dimethylaminodiborane

Molecular weight = 70.756, °K = °C + 273.16°

<i>S</i> ₁₉₀ , Debye-----	abs j deg ⁻¹ mole ⁻¹
$\Delta S_{190-190^\circ}$, solid-----	1.9
$\Delta S_{190-220^\circ}$, solid and liquid, including transitions-----	112.3
$\Delta S_{220-271.60^\circ}$, liquid-----	63.3
	31.2
<i>S</i> of the liquid at 271.60° K-----	208.7 ± 0.6
ΔS , vaporization, 30,119/271.60-----	110.9 ± 0.1
ΔS , gas imperfection-----	0.1
ΔS , compression to 1 atm, <i>R</i> ln (94.3/760)-----	-17.4 ± 0.0
<i>S</i> ideal gas at 1 atm and 271.60° K-----	302.3 ± 0.6

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